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B329 B32Y B331 B333 B335 B337 B339 B33X B349  
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B50Y B511 B513 B515 B517 B519 B51X B528 B52Y  
B531 B533 B535 B537 B539 B53X B549 B559 B610  
B611 B612 B616 B619 B620 B621 B624 B627 B62X  
B62Y B635 B63Y B661 B663 B665 B667 B669 B68X  
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GB A 2091294	GB 1436450	GB 1133397
GB A 2060394	GB 1430516	GB 1115055
GB A 2047748	GB 1427674	GB 1053151
GB A 2010920	GB 1412998	GB 0681484
GB 1542299	GB 1350720	GB 0224836
GB 1491156		

(58) Field of search

C7A  
C7F

(54) A process for plating an article with a gold-based alloy and an alloy therefor

(57) A dry ionic process for gold plating substrate articles 5 comprises suspending an article from a holder 2 in a vacuum chamber 1 above a heated bath of a gold-based plating alloy 3 and applying a voltage from an electrical supply 4 between the articles 5 and the bath 3 to deposit vapour of the alloy. The invention lies in the use in the bath of a gold-based alloy containing at least one of the following alloying metals:-

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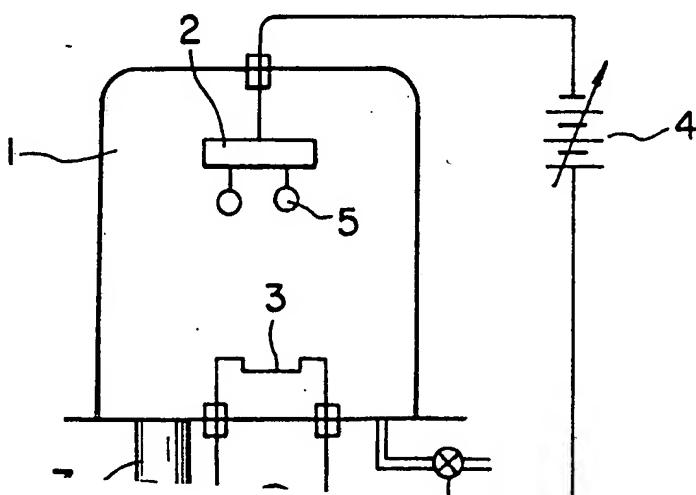
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Front page, Heading (72) Inventors for Hiswo Ahinomiya read Hideo Shinomiya  
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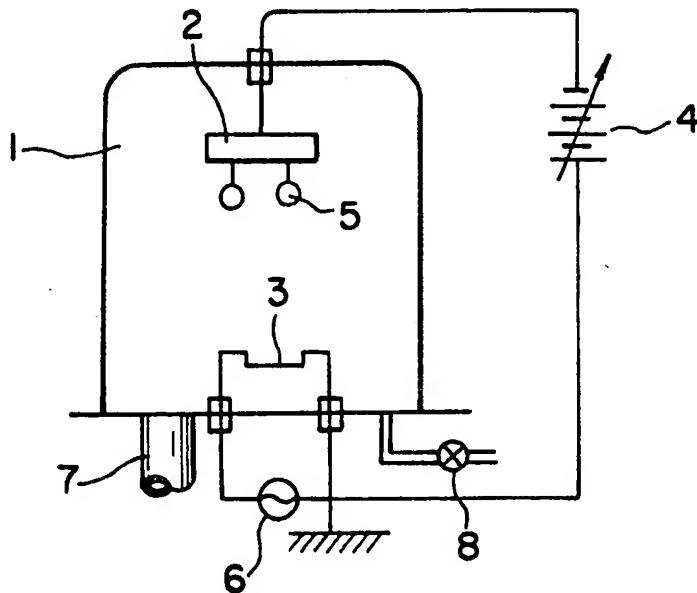
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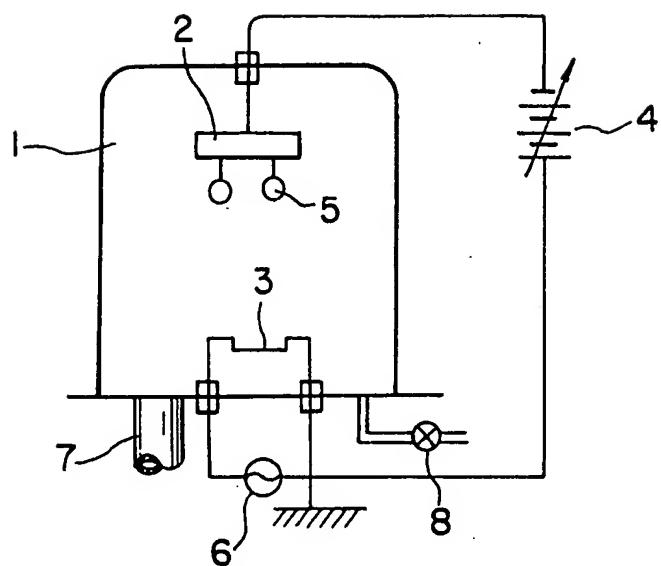
The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

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process can be carried out using a single alloy bath instead of using two or more different baths from which single metals are vaporized simultaneously and in this way various difficulties previously encountered are avoided. Despite the simplification of the process, the plating obtain is satisfactory in all respects including the control of the colour tone of the plated surface and the corrosion resistance and adhesion strength of the plating.

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## SPECIFICATION

## A process for plating an article with a gold-based alloy and an alloy therefor

5 The present invention relates to a process for plating an article with a gold-based alloy in order to provide, for example, a stable decorative coating film of a gold-based alloy of bright golden tone on to the surface of a metal article. The invention also relates to an alloy suitable for use in the process. 5

10 It is very common to apply a plating or coating film of a decorative golden metal or alloy to the surface of watch cases, watch straps, spectacle frames, personal ornaments, embellishments and the other decorative articles with the object not only of improving the aesthetic appearance of the articles but also to increase the corrosion resistance of the surface thereof. As is well known, such plating, which is referred to subsequently as gold plating, is rarely undertaken with pure gold but in most cases with a gold-based alloy mainly composed of gold. Therefore, the 10

15 colour tone of the plating differs a little in dependence on the composition of the gold-based alloy so that difficulties are sometimes encountered in constantly and reproducibly obtaining a gold plating having a colour tone which is quite satisfactory from the aesthetic point of view. 15

20 Gold plating of an article is performed either in a wet process or in a dry process and the traditional wet process is generally being replaced by a dry process such as vacuum vapour deposition, ion plating and other techniques carried out in the vapour phase by virtue of the 20 versatility of dry processes in respect of the materials of the substrate articles including those to which the wet process is not applicable. For example, stainless steels and titanium or titanium-based alloys, which can be gold-plated only with great difficulties by the wet process, can be easily plated with gold by a dry process using a gold-based alloy.

25 The conventional gold-plating technique using the dry process is usually performed in the following manner:— Two heating vessels are placed in a vacuum chamber and contain gold and an alloying metal, e.g. cobalt and titanium. The vessels are separately heated to effect vaporization of the metals so that the vaporized metals are simultaneously deposited on the surface of a substrate article in the vacuum chamber to form an alloy of gold and the alloying 25

30 metal in situ. In this technique of simultaneous vaporization and deposition of gold and an alloying metal, the two heating vessels must be heated independently from each other to keep the gold and the alloying metal at different temperatures since the vaporization characteristics differ from metal to metal. Although the heating means for these heating vessels is not particularly limitative, preferred means therefor are electric resistance heating and ion beam 30

35 heating from the standpoint of convenience. It is of course optional that the two vessels are heated by the same kind of heating means or by different kinds of heating means from each other. In this dual vaporization method, at any rate, it is very important that the heating intensities on the two vessels are accurately and exactly controlled along with the exact control of the vacuum in the chamber since otherwise reproducibility cannot be obtained in the colour 35

40 tone of the gold-plating which is influenced even by the slightest change in the relative vapour pressures of the gold and the alloying metal. 40

45 Accordingly, it is highly desirable that a dry process for gold-plating should be able to be performed using a single pre-alloyed gold-based alloy but no such alloy has until now been found which ensures the practicality of the process and satisfies the vapour requirements for such an alloy, even though gold-plating by the use of pure gold involves no such problems. The 45

50 requirements which a gold-based alloy suitable for dry-process gold plating should satisfy are that:—

(1) the composition of the alloy should be able to be kept constant throughout the process of vaporization, i.e. the gold and the alloying metal or metals should vaporize at rates which are exactly proportional to the relative contents thereof in the alloy which forms the source of vaporization; 50

(2) the colour tone of the gold plating obtained by use of the alloy should be able to be controlled from yellowish gold to reddish gold according to need by modifying the composition of the alloy;

55 (3) the alloy should have a melting point in the range of from 1000 to 1200°C; 55

(4) the alloy should be non-reactive or little reactive at the process temperature with the material of the heating vessel which is usually tungsten;

(5) the gold-plating film formed of the alloy should have high corrosion resistance;

(6) the overall corrosion resistance of the thus gold-plated article should also be good;

60 (7) an aesthetically acceptable golden colour tone should be obtained of an alloy with a gold content which is as low as possible in view of the great cost of gold in comparison with the alloying metals; and

(8) the alloy should be sufficiently malleable and ductile to enable it to be worked into thin plates or fine wires.

65 In view of the above described difficult requirements in dry-process gold plating using a single 65

gold-based alloy, the recent trend of the gold plating has been to use titanium nitride, tantalum carbide, combinations of titanium carbide and titanium nitride and other non-metallic plating materials although such a process is not entirely satisfactory in respect of the colour tone of the plating and the cost of processing. In particular, a method is disclosed in Japanese Patent 5 Publication No. 54-2942 in which a double or triple layered surface film is provided on the substrate surface by the deposition of gold and titanium on an underlying film of titanium nitride. This process is also not free from the problem of obtaining good reproducibility of the colour tone of gold plating and thus badly affects the yield of acceptable products. In particular, these prior art processes are disadvantageous in respect of the versatility in the colour tone of 5

10 the gold plating which should be able to be modified from yellowish gold to reddish gold to impart highly decorative effects to and in compliance with the diverse requirements of the users of watch cases and straps, spectacles frames and other decorative articles. 10

It is therefore an object of one aspect of the present invention to provide an improved process for the dry-process gold plating of decorative articles, which does not depend on the dual 15 vaporization techniques used in the prior art involving separately vaporizing gold and an alloying metal, but instead uses a single pre-alloyed gold-based alloy. 15

An object of another aspect of the present invention is to provide a gold-based alloy which is suitable for use as a plating alloy which is subjected to vaporization in dry-process gold plating of a decorative article. 20

20 Thus, according to one aspect of the present invention, a dry process for providing a gold plated layer on the surface of a substrate article comprises holding the substrate article in a vacuum chamber above a heated bath in the chamber of a gold-based alloy containing at least one of the following alloying metals:—chromium, iron, cobalt, nickel, palladium and copper, the content of the or each alloying metal being, for the chromium, iron, cobalt and nickel in the 25 range of from 1% to 10% by weight, and for the palladium and copper in the range of from 0.5 to 20% by weight and the balance of the alloy except for impurities being gold, heating the alloy in the bath to a temperature in the range of from 1000° to 1500°C, and applying a voltage between the alloy and the substrate article to deposit vapour of the alloy on to the 25 surface of the substrate article by ion plating. 25

30 The invention also consists, according to another of its aspects, in a gold-based alloy for use in the process in accordance with the invention, the alloy containing at least one of the following alloying metals:—chromium, iron, cobalt, nickel, palladium and copper, the content of the or each alloying metal being, for the chromium, iron, cobalt and nickel in the range of from 1% to 10% by weight, and for the palladium and copper in the range of from 0.5% to 20% by weight 35 and the balance of the alloy except for impurities being gold. 35

Preferably the alloying metal or metals are chromium, cobalt, nickel and/or palladium.

Some examples of processes and of alloys in accordance with the invention will now be described with reference to the accompanying drawing which is a diagram of apparatus including an electrical circuit used in carrying the process. 40

40 As is understood from the above description, the essential scope of the invention is in the use of a unique gold-based alloy which has never been used or tested as a gold-based plating alloy in the dry-process gold plating. The gold-based alloy of the invention can be prepared in advance by melting together the respective component metals taken in a predetermined proportion and the thus preformed alloy is shaped into a thin plate or wire to be placed and 45 melted in a heating boat inside the dry-process plating apparatus. 45

According to the above described method, the color tone of the gold plating can be freely and delicately modified depending on the kind and content of the alloying metal or metals.

According to the discovery of the inventors, for example, palladium in the alloy has an effect of imparting a pinkish tint to the gold-based alloy though dependent on the content thereof, cobalt 50 and nickel in the alloy have an effect of imparting paleness to the golden color of the alloy and chromium is effective when a lightly to deeply reddish golden color is desired of the gold-based alloy. 50

55 It is also noteworthy that the color tone of the gold-plated surface obtained using the above described gold-based alloy of the invention in the dry process is sometimes quite different from that of the alloy in mass and a possibility is provided to obtain a fancy color tone which is not imaginable from the color of the alloy in mass so that the aesthetic effect obtained by the invention is very great. 55

60 In the inventive gold-based alloy, the content of each of the alloying metals should be within the specified range. The kinds of the alloying metals have been selected specifically after an elaborate and extensive experimentation in which the alloy composition of the vaporized and deposited gold plating layer formed under a predetermined pressure of vacuum by use of a gold-based alloy containing a particular alloying metal was carefully analyzed and compared with the alloy composition in mass to determine the kind and content of the alloying metal in the alloy in mass to give a plating layer of the alloy having a composition which is the same as or 65 close to that in the alloy in mass as the vapor source. For example, silver, which is the most 65

conventional alloying metal in gold-based alloys, did not pass this test due to the much larger velocity of vaporization thereof than gold resulting in a gradual shift in the color of the deposited plating layer from silvery gold to yellowish gold inherent to pure gold per se when a gold-silver alloy was used in a dry-process gold plating. In short, it is one of the essential requirements that

5 the vaporization of the alloying metal should take place at such a velocity relative to that of gold as to be proportional to the content of the alloying metal in the alloy under vaporization as the vapor source. The above mentioned alloying metals, i.e. chromium, iron, cobalt, nickel, palladium and copper, well satisfy this requirement.

In connection with the preferable content of each of the alloying metals in the inventive gold-based alloy, cobalt forms a solid solution with gold at elevated temperatures up to a content of 10 about 8.4% by weight but hardly forms a solid solution at room temperature while addition of 1% by weight or more of cobalt to gold imparts a somewhat reddish tint to the pure gold but addition of 10% by weight or more of cobalt to a gold-based alloy is undesirable due to the whitish appearance of the deposited alloy layer with disappearance of the golden color. This is 15 the reason for the 1 to 10% limitation of the cobalt content in the alloy together with the fact that a gold-based alloy containing 10% by weight or more of cobalt is detrimental to the 15 corrosion resistance of the deposited gold plating layer.

Nickel as an alloying metal in gold can form solid solutions in all proportions but addition of 10% by weight or more of nickel in a gold-based alloy is undesirable due to the platinum-like 20 color tone of the alloy. Nickel is effective in modifying the color tone of the gold-based alloy even in an amount of 1% by weight or more to impart the alloy with a color tone resembling that of a ternary alloy of gold, silver and copper.

Palladium behaves in a manner somewhat similar to nickel and also forms solid solutions in all proportions. Different from nickel, however, palladium has a trend to impart a reddish tint to the 25 gold-based alloy even in an amount of 1% by weight or more while a gold-based alloy containing 20% by weight or more of palladium is no longer golden but pale reddish white so that the content of palladium in the inventive gold-based alloy should be in the range from 1 to 20% by weight.

Chromium forms a solid solution with gold up to a content of about 7% by weight. 30 Characteristically, the color of the vapor-deposited layer of the gold-chromium alloy is reddish gold and quite different from that of the alloy in mass and also delicately different from the reddish golden color obtained of the gold-palladium alloys. This effect of the addition of chromium is apparent even in a chromium content of 1% by weight while the color tone obtained of a gold-chromium alloy of 10% by weight or more of chromium content produces a 35 whitish color on the vapor-deposited plating layer due to the predominant vaporization of chromium along with the less reproducible color tone.

Iron can form a solid solution with gold in a relatively large proportion at elevated temperatures and the effect obtained by the addition of iron levels off at an iron content of about 1% by weight. Iron is, however, less preferable among the alloying metals used in the 40 inventive gold-based alloys due to the adverse effect of iron on the corrosion resistance of the alloy. In particular, gold iron alloys containing 10% by weight or more of iron are hardly usable as the base alloy for gold plating due to the impractically low corrosion resistance and the poor reproducibility in the color tone of the plating layer.

Copper as an alloying metal used alone has a relatively small effect of modifying the color 45 tone of gold-based alloys although addition of copper in an amount of 0.5% by weight has an effect of imparting very beautiful and aesthetically acceptable reddish golden tint to the alloy. Addition of copper alone to gold in an amount in excess of 20% by weight is undesirable due to the predominant vaporization of copper to give a cupreous color to the deposited plating layer along with the great decrease in the corrosion resistance of the alloy. It is, however, 50 advantageous that copper is used as an alloying metal in combination with one or more of the other alloying metals, i.e. cobalt, nickel, chromium, iron and palladium, from the standpoint of the delicately modifiable aesthetic effect as well as cost saving owing to the reduction of the gold content in the alloy. In particular, alloying of gold with copper and chromium in combination is advantageous because the alloy of such a composition has a corrosion resistance 55 and the color tone approximating to those of 18-karat gold.

Any one of the above described gold-based alloys can be used as the vaporization source in the ion plating according to the invention. Particularly preferable are, however, the alloys of gold with one or more of the alloying metals selected from the group consisting of nickel, cobalt, chromium and palladium. The alloys should contain no other foreign metals possibly affecting 60 the color tone of the alloy excepting very small amounts of unavoidable impurity metals. When two or more kinds of the alloying metals are used in combination, the total amount thereof should preferably be 10% by weight or smaller in the alloy.

The process of ion plating according to the present invention can be performed in a variety of known methods including direct-current ion plating, multi-cathode ion plating and high 65 frequency-induced ion plating and the like using respective apparatuses therefor. The ion plating

method here implied also includes the process in which a metallic coating film is deposited on the substrate surface by the glow discharge within a vacuum chamber to form a plasma atmosphere in which the alloy is vaporized.

In carrying out the ion plating according to the invention, an alloy having a desired color tone 5 or capable of giving a deposited plating layer having a desired color tone is prepared in advance and the alloy shaped in the form of a plate or wire is put into a heating boat inside a vacuum chamber of the apparatus to be vaporized and deposited on the substrate surface to give a plating layer of the desired color. The color tone of the alloy or the plating layer of the alloy is of course dependent on the type and amount of the alloying metal or metals. Although the color 10 tone of the alloy is changed continuously with the change in the content of the alloying metal, the main component in the alloy should of course be gold and the content of gold in the alloy should be in the range from 60 to 90% by weight in so far as the object of the inventive method is in the gold plating at any rate, the balance of gold being one or more of the alloying metals of nickel, cobalt and chromium each up to 10% by weight and palladium up to 20% by 15 weight and unavoidable impurity metals. The kind or combination and amount of the alloying metal or metals should be carefully selected in consideration of the respective effects of the metals described above on the color tone of the gold-based alloy.

In practicing the ion plating according to the invention, the gold-based alloy is mounted on a heating boat of, for example, tungsten which is placed in the vacuum chamber of an apparatus 20 for ion plating and, while the atmosphere inside the vacuum chamber is kept at a pressure of  $10^{-2}$  to  $10^{-4}$  Torr of an inert gas, heated at a temperature in the range from 1000 to 1500°C with application of a voltage of, for example, 0.5 to 1 kilovolt between the substrate article and the alloy in the boat. In this manner, the gold-based alloy under heating in the boat is vaporized and deposited on the surface of the substrate forming a plating layer of the alloy having 25 substantially the same composition as the alloy in the boat as the vaporization source.

Different from the case of the binary vaporization and deposition using two separate heating boats for gold and an alloying metal, no strict control of the vaporization velocity of the alloy is required in this case. It is, however, preferable that the velocity of vaporization of the gold-based alloy should be controlled so that the plating layer on the substrate surface is formed at a rate in 30 the range from 5 to 50 nm of the thickness per second from the stand-point of the quality of the plating layer and the commercial value of the plated article due thereto. The velocity of vaporization of the alloy can be controlled by suitably selecting the vacuum pressure inside the chamber and the heating temperature of the alloy in the boat.

The final thickness of the plating layer thus formed on the substrate surface is usually in the 35 range from 0.2 to 1  $\mu\text{m}$  according to desire. It is desirable that the amount of the alloy taken in the heating boat should be in excess somewhat over the exact amount of the alloy to be deposited on the substrate surface in a layer of the desired thickness. When, on the contrary, the amount of the alloy taken in the heating boat is exactly the same as that of the amount of the plating layer on the plated substrate surface, the composition of the vaporizing alloy at the 40 very late stage of the vaporization process may be more or less different from that at the beginning stage resulting in the deviation of the color of the plating from the desired one. In this regard, the vaporization of the alloy in the heating boat should be terminated when the remaining amount of the alloy in the boat has decreased to 5% or more or, preferably, 10% or more or, more preferably, 20% or more of the amount of the alloy initially taken in the heating 45 boat.

The substrate article on which the plating layer of the gold-based alloy is formed by the techniques of ion plating as described above is usually metallic such as watch cases, watch straps, personal ornaments and the like. Although a sufficiently high adhesive strength can be obtained between the plating layer and the metallic substrate surface when the substrate has 50 been thoroughly cleaned before ion plating, it is of course optional in order to further improve the adhesive strength therebetween that the substrate surface is subjected to a suitable pretreatment such as a primary plating with a metal or alloy different from the inventive alloys, oxidation treatment, nitriding treatment and the like. When the substrate article is non-electroconductive such as glass, ceramics and the like, it is necessary that the substrate surface 55 should be provided with an undercoating of an electroconductive material.

In the next place, the method of the invention is described in further detail with reference to the accompanying drawing.

The figure is a schematic illustration of the apparatus and electric circuit for practicing the method of the present invention by the direct-current ion plating, in which a substrate holder 2 which also serves as a cathode and a heating boat 3 having a heating means on the lower surface are provided inside a vacuum chamber 1. The substrate holder 2 and the heating boat 3 are respectively connected to a direct-current power source 4, the heating boat being the anode. The substrate articles 5 are held by the substrate holder 2 to face the heating boat 3 below. The heating boat 3 is heated and controlled at a desired temperature by means of the heating power 65 source 6.

With the substrate articles 5 after thorough cleaning mounted or hung on the substrate holder 2 and a predetermined amount of the gold-based alloy taken in the heating boat 3, the vacuum chamber 1 is evacuated through the vacuum duct 7 to a pressure of, for example,  $2 \times 10^{-5}$  Torr or below by operating a vacuum pump (not shown in the figure). Thereafter, a small 5 volume of argon gas is introduced by opening the gas inlet valve 8 so as to bring the pressure inside the chamber to about  $5 \times 10^{-5}$  Torr and the substrate surface is subjected to bombardment by applying a DC voltage of 100 to 1000 volts to the substrate holder 2 by means of a DC power source 4 to be ready for the ion plating which is undertaken by increasing the pressure inside the chamber to  $10^{-2}$  to  $10^{-3}$  Torr by the introduction of argon gas and 10 heating the gold-based alloy in the boat up to a temperature of 1300°C or higher by means of the resistance heater below the boat energized by the power source 6 so that the ions of the alloy metals are vaporized from the heated alloy and attracted by and deposited on the substrate surface to form a plating layer of the alloy. 15

Following are the examples to illustrate the inventive gold-based alloys and the method of the 15 invention in more detail. 15

**Example 1.**

Gold-based alloys were prepared each by melting together gold and 1 to 4 of the alloying metals according to the formulation given in Table 1 in a zirconia crucible heated in a high 20 frequency induction furnace under an atmosphere of argon and cast into an ingot which was worked into a test piece of 0.5 mm by 20 mm by 25 mm by repeating annealing and rolling. 20

The color tones of the thus prepared test pieces of the alloys were visually examined and compared with pure gold and the results are shown in Table 1. As is clear therefrom, the golden color of pure gold is delicately and differently modified by the addition of the respective alloying 25 metals to be in compliance with aesthetic desires for the color tone. In this test, those alloys containing the alloying metals other than copper in an amount over 10% by weight were omitted because they had a whitish color not to meet the object of the invention of gold plating. 25

The above prepared test pieces of the gold-based alloys were then subjected to the test of the corrosion resistance by dipping at 40°C for 96 hours in a simulated perspiration used for the 30 corrosion test of noble metal-containing alloys and containing the solutes of 0.9 g/liter of sodium chloride, 0.8 g/liter of sodium sulfide, 1.7 g/liter of urea and 1.7 ml/liter of lactic acid and having a pH of 3.6 by adjusting with 0.2 g of ammonia water. The results obtained by the visual examination of the surface of the test pieces are given in Table 1. 30

**35 Example 2.** 35

The gold-based alloys No. 1 to No. 10 prepared in the preceding example were subjected to the preliminary test of ion plating.

Thus, SUS 316 grade stainless steel plate of 1 mm thickness was cut into pieces of each 20 mm by 30 mm wide followed by mirror-polishing by buffing and washing with an organic 40 solvent and 10 pieces were placed on the substrate. 40

**Table 1**

45	Alloy No.	Content in alloy, % by weight							Color	Corrosion resistance	45
		Au	Pd	Co	Ni	Fe	Cu	Cr			
50	1	95	5	—	—	—	—	—	Pinkish	Good	
	2	92	—	8	—	—	—	—	Light yellowish	Slight color change	50
	3	95	—	—	5	—	—	—	Ditto	Good	
	4	96	—	—	—	4	—	—	Yellowish	Some spots	
	5	97	—	—	—	—	3	—	Reddish	Good	
55	6	94	—	—	—	—	—	6	Light reddish	Good	55
	7	75	—	—	8	—	10	7	Ditto	Good	
	8	75	—	3	5	—	15	2	Yellowish	Good	
	9	75	1	—	—	—	20	4	Pinkish	Good	
60	10	85	15	—	—	—	—	—	Light pinkish	Good	
	Pure gold	100	—	—	—	—	—	—	Pure golden	Good	60

holder of an ion plating apparatus to serve as the cathode. 65 On the other hand, the gold-based alloy in the form of a 0.5 mm thick plate was cut into 65

pieces of suitable size with scissors and about 5 g of the alloy pieces were put into the tungsten-made resistance-heating boat in the vacuum chamber of the ion plating apparatus. Then, the vacuum chamber was evacuated to a pressure of  $2 \times 10^{-5}$  Torr followed by the introduction of argon gas so that the pressure inside the chamber was brought to  $5 \times 10^{-4}$  Torr.

5 In this atmosphere of low pressure argon, an electric voltage of 1 kilovolt was applied to the stainless steel substrate plates to effect cleaning of the surface thereof by bombardment and the tungsten boat was heated by passing electric current to melt and vaporize the alloy contained therein and deposit the alloy vapor on the surface of the substrate plates. The electric voltage and current in this ion plating process were 30 volts and 250 amperes, respectively, and the ion 5

10 plating was continued to give a plating layer of 1 to 2  $\mu$ m thickness. It should be noted that the rate of current increase delicately influences the color tone of the deposited alloy plating layer as a result of the difference in the velocity of melting to vaporization even by use of a gold-based 10 alloy of the same composition and under the same ultimate electric conditions for the ion plating.

15 For example, increase in the vaporization velocity of an alloy of gold and palladium had an effect of imparting a reddish tint to the deposited plating layer while decrease in the vaporization velocity of the same alloy imparted a pinkish tone to the reddish golden surface of the deposited layer.

20 The thus plated stainless steel plates were subjected to the test of the adhesion strength or peelability of the plating alloy layer to the substrate surface by bending the plate at right angle and visually examining the condition of the plating layer along the bent line. The results were that the adhesion of the plating layer to the substrate surface was quite satisfactory without exfoliation in all of the test pieces prepared by use of the gold-based alloys No. 1 to No. 10.

25 The ion-plated stainless steel plates were further subjected to the test of corrosion resistance by dipping in the simulated perspiration in the same manner as in the corrosion test of the alloy plates per se described in Example 1. The results are shown in Table 2 below together with the color tones of the plating layers.

30 Table 2

Alloy No.	Color of plated surface	Corrosion resistance	30
35 1	Pinkish golden	No discoloration	
2	Somewhat pale yellowish golden	Ditto	35
3	Like Au-Ag-Cu 18-karat gold	Ditto	
4	Ditto	Ditto	
5	Reddish golden	Ditto	
6	Pale reddish golden like TaC	Ditto	
40 7	Slightly reddish pale yellowish golden	Ditto	40
8	Yellowish golden	Slight discoloration but acceptable	
9	Pale reddish golden	Ditto	
10	Pale pinkish golden	No discoloration	45

45 Example 3.

50 A nickel-plated watch case of Bs alloy having an area of the lower surface of about  $20 \text{ cm}^2$  was washed with methyl alcohol and acetone followed by drying was mounted on the substrate holder of the ion plating apparatus. On the other hand, 10 g of a 95:5 by weight alloy of gold and nickel were taken in the heating boat of the apparatus and the vacuum chamber was evacuated to a pressure of  $2 \times 10^{-5}$  Torr followed by the introduction of argon gas to bring the pressure inside the chamber to  $5 \times 10^{-4}$  Torr. In this condition of the atmosphere, a DC voltage of 1000 volts was applied to the substrate to clean the surface by bombardment. Thereafter, the 55 pressure inside the chamber was further increased to  $3 \times 10^{-3}$  Torr by introducing an additional volume of argon gas and the gold-based alloy in the heating boat was heated to about  $1500^\circ\text{C}$  so that the alloy was vaporized and deposited on the lower surface of the watch case. The rate of vaporization was controlled so that the plating layer on the substrate was deposited at a rate of about 5 nm per second and the plating was continued for 3 minutes. The final thickness of 60 the plating layer was 450 nm.

65 In this manner, 100 watch cases were successively subjected to the ion plating. When the ion plating of the 100th watch case had been completed, the remaining amount of the gold-based alloy in the heating boat was about 3 g. It was found that the first-plated and the last-plated watch cases had substantially the same appearance of beautiful golden color. The corrosion 65 resistance and abrasion resistance of the plating were quite satisfactory in both of the first-plated